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Abstract

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N.M.R. SPECTRA AND EBULLIOSCOPY OF LITHIUM ALKOXIDES

The study of the structure of lithium alkoxides by various physicochemical methods has shown that these compounds are associated and that the O—Li bond in the complex has a predominantly covalent character (1-3). It was suggested that the existence of the indicated complexes is connected with the ability of the O—Li groups of compounds of the type R—O—Li to form chemical bonds with one another by means of donor-acceptor interaction, and also through multicenter molecular orbitals realized owing to the presence of three free $2P$-orbitals of the Li atom.

The present work was undertaken with the aim of further studying the structure of compounds of the type R—O—Li and of experimentally verifying the considerations advanced concerning the character of the O—Li bond in the complex. By the ebullioscopic method it was found that tert-C_4H_9OLi is associated in solutions in cyclohexane with concentrations in the range $0.01—0.07\,N$, with an association factor equal to 6.4 ± 0.7, and in solutions in benzene with concentrations $0.001—0.08\,N$, with an association factor equal to 9.4 ± 0.9. If it is assumed that the simplest associate of tert-C_4H_9OLi is a trimer (a planar or nearly planar six-membered ring), then the hexamer and nonamer may be imagined as being built up in a "stack," respectively from 2 or 3 trimers, similarly to the way complexes of compounds of the type R—Li are built (4).

Table 1

Substance	Second moment $\langle \Delta H_2^2 \rangle$ Hexp., G^2	Second moment $\langle \Delta H_2^2 \rangle$ Htheor., G^2	Second moment $\langle \Delta H_2^2 \rangle$ Liexp., G^2
tert-C_4H_9OLi	1 ± 0.1	0.9	1.4 ± 0.1
n-C_4H_9OLi	16.8 ± 0.8	9.3	–

Such a structure of complexes of the compounds R—O—Li and R—Li, apparently, is determined by the nature of the Li atom and corresponds to the most effective utilization of free orbitals. However, in the structure of the complexes of these compounds there are substantial differences: the simplest (less stable) associate for compounds of the type R—Li is the dimer, whereas for R—O—Li, apparently, it is the trimer. The differences in the structure of these complexes are probably connected with the electron-donor properties of the oxygen atom.

We have obtained N.M.R. spectra of crystalline tert-C_4H_9OLi and n-C_4H_9OLi for H^1 and Li^7, as well as high-resolution proton spectra for solutions of tert-C_4H_9OLi in benzene and cyclohexane.

The second moments of the lines obtained from the N.M.R. spectra of H^1 and Li^7 in crystalline tert-C_4H_9OLi and n-C_4H_9OLi are given in Table 1.

The value of the second moment ΔH_2^2 of the H^1 line for tert-C_4H_9OLi is close to the theoretical value. This value was calculated on the assumption that the whole CH_3 group rotates around the C—C bond; that there is rotation around the C—O bond; that the influence of neighboring CH_3 groups on one another is not taken into account (5); and that the Li^7 nuclei are located no closer than at a distance of 3.5 Å from the rotating CH_3 groups (the value 3.5 Å was obtained on the assumption that, for the $(CH_3)_3CO$ group, the usual geometry is realized and the C—O—Li angle is taken to be 120°). The influence of Li nuclei on the N.M.R. H^1 line was taken into account analogously to the way this was done in work (6). From the value of the second moment of H^1 in tert-C_4H_9OLi it may be concluded that the radicals of the molecules do not interact with one another. On this basis it may be concluded that the complexes of crystalline tert-C_4H_9OLi are built analogously to its complexes in solutions and vapors (1-3). Such

The similarity of complexes in different aggregate states can be explained by the fact that the framework of O—Li groups is surrounded by "umbrellas" of CH_3 groups.

The narrow NMR line of Li^7 in crystalline tert.-C_4H_9OLi seems unexpected, since the Li^7 nucleus has a quadrupole moment and a covalent bond, which gives asymmetry in the distribution of the electronic charge on the Li^7 nucleus, would seemingly have to broaden the line strongly. The small width of the Li^7 line can be explained only by the presence of high symmetry of the electronic environment, and not by averaging of the field due to rotation of the CH_3 groups (since the distance from H^1 to the Li^7 nucleus in this case is about 3.5 Å). The high symmetry of the electronic environment (and it is higher than in LiCl, since the NMR of Li^7 in crystalline LiCl gives a line of greater width) can be explained, as in the case of an ethyllithium solution ([7]), by a very effective generalization ("exchange") of the valence electrons of the O—Li and C—Li groups as a result of the formation of multicenter molecular orbitals, as was assumed earlier ([8]).

The value of the second moment of the H^1 line for n-C_4H_9OLi was calculated under the assumption that the CH_2 groups are hindered, while only the CH_3 groups rotate, since the spectrum gives two lines—a narrow and a broad one with an intensity ratio of 1 : 2. The calculated value of the second moment and the value obtained experimentally differ by 7.5 G^2, which constitutes the contribution to the second moment from intermolecular interaction. This difference in the second moments indicates that the radicals are located close to one another. The NMR line of Li^7 for n-C_4H_9OLi could not be observed because of strong broadening.

It had previously been suggested that the simplest compound of this series, CH_3OLi, is either a purely ionic compound or a polymer (^{9}, ^{10}). If one assumes that the intermolecular bond in n-C_4H_9OLi has the same nature as in CH_3OLi, then the NMR data for Li^7 obtained for n-C_4H_9OLi refute the first of the proposed assumptions about the nature of the bond, since in the case of an ionic bond one should expect a narrow Li^7 line, and they confirm the second. If in the case of n-C_4H_9OLi the molecule is a polymer, then strong interaction of the radicals is ensured and the H^1 line is broadened. The Li^7 line is also broad, since the environment of the Li^7 nucleus by O atoms is asymmetric. In the case of formation of multicenter orbitals, such as in tert.-C_4H_9OLi, we should have expected a narrow Li^7 NMR line. Thus, for compounds of the type n-C_4H_9OLi, donor–acceptor interaction plays the main role in complex formation.

The high-resolution proton magnetic resonance spectrum (of the order of $4 \cdot 10^{-8}$) of a solution of tert.-C_4H_9OLi in benzene consists of one line, shifted toward higher fields relative to benzene by $(6.02 \pm 0.06) \cdot 10^{-6}$. The spectra were recorded in the concentration range 0.14–0.3 N; no change in the shift was observed. In cyclohexane solution there is also a single line; its shift toward higher fields from cyclohexane is $(0.24 \pm 0.03) \cdot 10^{-6}$, which agrees with the data for the benzene solution of tert.-C_4H_9OLi. For comparison, the shift of the line corresponding to the CH_3 group for tert.-C_4H_9OH was measured under the same conditions. It is equal to $(6.20 \pm 0.06) \cdot 10^{-6}$. It is known, however, that for most compounds of the type C_2H_5X, for substituents X within one row of elements, a change in the electronegativity of substituent X by 0.4 corresponds to a change in the shift of the CH_3 group, separated from the substituent by two C—C bonds, by $0.1 \cdot 10^{-6}$ (^{11}, ^{12}). It is also known that a change in the electronic charge by 1 gives a change in electronegativity of 0.4 (^{13}, ^{14}). Thus, if we were dealing with purely donor–acceptor bonding, the largest shift would occur if the oxygen atom donated even two of its electrons from two lone pairs to the neighboring two Li atoms; this would give a shift of $\sim 0.07 \cdot 10^{-6}$, since in our case each molecule contains three groups-

the CH_3 group. This cannot explain the observed shift of $0.18 \cdot 10^{-6}$ between the lines corresponding to the CH_3 groups in tert-C_4H_9OLi and tert-C_4H_9OLi, and therefore donor–acceptor interaction cannot be regarded as the principal mechanism of bonding in the tert-C_4H_9OLi complex.

The motion of electrons over multicenter orbitals, on the outside of which the radicals are located, can explain the magnitude of the shift, since experimentally a tendency has been noted for signals from H atoms bound to any rings to appear in the region of weaker fields, compared with H^1 atoms in chain molecules (the ring-current effect). For example, the shift between the CH_2 groups in hexane and cyclohexane is $0.3 \cdot 10^{-6}$ (^{12}).

This shift of $0.18 \cdot 10^{-6}$ for tert-C_4H_9OLi can be explained by the same effect, if one assumes that the tert-C_4H_9OLi complex is constructed in the form of a "stack" of trimers. It need only be taken into account that the distance to the protons of interest to us will be greater than in the case of cyclohexane. In cyclohexane the distance from the center of the ring to the protons is 2.6 Å, whereas in our case it will be about 4 Å, and this will give a shift of $\sim 0.1 \cdot 10^{-6}$. Obviously, the magnitude of this shift should be greater than the value obtained, since in the case of tert-C_4H_9OLi the O–Li bonds will be less localized than the C–C bonds in cyclohexane. If the electrons in the multicenter orbital are regarded as completely delocalized and "free," then a calculation by the ring-current method ([12,15]), under the condition that 6 electrons are delocalized in the molecular orbital of the trimer, gives a shift of $0.7 \cdot 10^{-6}$.

One should not expect substantial changes in the proton NMR spectra of tert-C_4H_9OLi complexes of different complexity, since the groups containing protons in such complexes are situated far from the framework of the complex. Differences may be expected in high-resolution Li^7 NMR spectra, which will be the subject of further study.

It is also possible that the characteristic features of the IR absorption spectra of tert-C_4H_9OLi are due to vibrations of the simplest associate, say a trimer. Then the preservation of the form of the IR absorption spectra of this compound in crystals, solutions, and vapors can apparently be explained by assuming that the bonds between trimers in the complexes are weaker than the bonds in the ring of the trimer. Thus, in the case of polymeric association, in crystals of the n-C_4H_9OLi type, bonding is apparently effected mainly by donor-acceptor interaction; under these conditions the maximum coordination of the lithium and oxygen atoms is achieved. In complexes of the tert-C_4H_9OLi type, the bonds are effected predominantly through the formation of multicenter orbitals, and donor-acceptor interaction no longer plays the principal role.

The different type of bonding evidently also explains the difference in the chemical behavior of these compounds: solubility, volatility, etc. ([1,2]).

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REFERENCES

1. A. P. Simonov, D. N. Shigorin et al., DAN, **136**, 634 (1961).
2. A. P. Simonov, D. N. Shigorin et al., DAN, **141**, 665 (1961).

3. A. P. Simonov, D. N. Shigorin et al., Izv. AN SSSR, OKhN, 1962, No. 1.
4. A. N. Rodionov, D. N. Shigorin et al., DAN, **143**, 137 (1962).
5. E. Rochow, H. Le Clair, *Inorg. and Nucl. Chem.*, **1**, 92 (1955).
6. V. V. Moskalev, *Fiz. tverd. tela*, **3**, 3046 (1961).
7. T. L. Brown, D. W. Dickerhoof, D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).
8. D. N. Shigorin, *Hydrogen Bonding*, London, 1957, p. 201.
9. P. J. Wheatley, *J. Chem. Soc.*, 1960, 4270.
10. H. Dannen, J. Krausse, *Zs. Chem.*, **1**, 27 (1961).
11. J. R. Cavanaugh, B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).
12. J. Pople, W. Schneider, H. Bernstein, *High-Resolution Nuclear Magnetic Resonance Spectra*, IL, 1962.
13. L. Pauling, *The Nature of the Chemical Bond*, Moscow–Leningrad, 1947.
14. S. S. Batsanov, *Electronegativity of Elements and Chemical Bonding*, Novosibirsk, 1962.
15. J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

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